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REMOVAL OF VARIOUS METAL IONS IN WATER BY DIFFERENT PRE-TREATMENTS OF FLY ASH

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Abstract

Rapid urbanisation in Malaysia has accelerated water pollution in rivers and other water sources, causing irreversible harm to the ecosystem. In view of that, this study aimed to work on using fly ash to address certain heavy metal components (chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn)) present in polluted water. The experiment employed three batches of fly ash. Two batches were treated with sodium hydroxide (NaOH-FA) and hydrochloric acid (HCl-FA), whereas one batch was left untreated (UFA). The three batches of adsorbents were examined by using a jar test after solutions containing 100 mg/L of Cr, Cu, Ni, and Zn ions were made. The results of various contact periods demonstrated that the fly ash had variable capacities for metal ion adsorption. The maximum adsorption of UFA was 79.958%(Cr), 80.814%(Cu), 81.580%(Ni), and 82.742%(Zn) while HCl-FA was adsorbing 77.148%(Cr), 82.546%(Cu), 78.896%(Ni), and 78.248%(Zn). NaOH-FA in this study was found to adsorb 80.828%(Cr), 79.230%(Cu), 81.692%(Ni), and 77.394%(Zn). Further to this, it was revealed that the Temkin Isotherm model was best fitted with the highest R^2 values (> 0.98). The negative value of the slope, B indicated that the adsorption is an endothermic process which leans towards physical adsorption. In conclusion, this study demonstrated the successful application of fly ash in water or wastewater treatment of metal ions.

Keywords: fly ash, metal ions, water treatment, adsorption, water pollution

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INTRODUCTION

Water is one of the most precious natural resources on earth. Even though freshwater makes up only less than 3% of the earth's surface, it is nonetheless frequently over-extracted and contaminated by humans due to their activities. As per the World Health Organization (WHO) guidelines, people should receive a minimum of 7.5 litres of treated water daily, with an immediate need for at least 15 litres during the initial post-impact period (WHO, 2023).

Malaysia is not an exception as it is also one of the countries grappling with challenges arising from water pollution (Habibullah et al., 2023). Despite having abundant water resources, we are still facing water disruption from time to time in some areas due to the illegal dumping of wastewater by irresponsible parties to their nearby rivers (Goi, 2020; Salleh et al., 2022). As stated by Othman et al. (2018), the rivers in Malaysia have been contaminated by heavy metals recently due to rapid urbanisation and industrialisation. The common heavy metals that are released by industrial wastes are zinc (Zn), lead (Pb), copper (Cu), iron (Fe), chromium (Cr), cadmium (Cd), manganese (Mn), and nickel (Ni) which are toxic and harmful to the environment and human health (Alsaffar et al., 2019). According to Feary and Cullinan (2019), these toxic heavy metals are commonly produced and discharged from metal refining factories, thermal power plants, petroleum refineries, battery industries, and smelting plants. The accumulation of these heavy metal contaminants in water not only affects human health with various kinds of diseases but also the growth reduction of plants and reduced breeding potential of adult fish. One of the examples, itai-itai disease found in Japan was due to the high concentration of cadmium (Cd) exposure and the symptoms of this disease that include bone pain and renal tubular dysfunction (Nguyen, 2020).

Regrettably, conventional municipal wastewater treatment lacks any designated process for removing heavy metals from the water. The conventional treatment mentioned here involved the primary settling and biological nutrient removal or activated sludge process (Sylwan and Thorin, 2021). In fact, there is a range of drawbacks to these conventional wastewater treatment systems, including high chemical consumption, releases of greenhouse gases, significant power consumption, and high operational and construction costs (Tan et al., 2023). Owing to this condition, various water and wastewater treatment methods are currently available and promoted in the market to remove different types of pollutants. These methods included membrane filtration, ion exchange, and adsorption. Amongst these methods, adsorption has become the most popular technique used due to its simplicity, effectiveness, and low cost. Many researchers are focusing on a variety of materials, particularly those that are natural and inexpensive, to explore their adsorption capabilities due to their inherent physical and chemical properties. These adsorbents often come from the

by-product of agricultural or industrial processes, and thus are readily available and economical. Examples of natural and low-cost adsorbents are ash, wood, clay, corn cob, fruit peel, wheat straw, starch graft, and moss (Ramesh, et al., 2016).

In Malaysia, there are about 43% of electricity is generated from coal-fired power plants (Mardi et al., 2023). During coal combustion, fly ash is one of the waste by-products of coal-fired electric power plants. According to Ghazali et al. (2019), Malaysia generates around 6.8 million tonnes of fly ash annually, while global production reaches approximately 750 million tonnes, and this is still continually increasing every year (Beddu et al., 2018). The main compositions that makeup around 90% of the fly ash are silicon dioxide (SiO₂), aluminium oxide (Al₂O₃), iron oxide (Fe₂O₃), and calcium oxide (CaO). Undoubtedly, fly ash has a strong adsorption capacity due to its porous structure and large surface area. However, only a small amount of fly ash has been widely adopted in the cement component for the concrete to improve its workability and avoid segregation (De Maeijer et al., 2020). Despite that, its utilisation remains marginal as compared to the overall yield. Several researchers used fly ash to remove the pollutants from the contaminated water. Based on the previous study by Nguyen et al., (2020), modified fly ash was tested and successfully removed a maximum of 97% and 90.80% of Cd²⁺ and Hg²⁺ ions respectively. Darmayanti et al. (2017) also claimed that fly ash was able to remove 24.9% to 93.9% of Cu ions by using 1 g/L to 10 g/L of fly ash. Besides, Eteba et al.(2021) observed that observed remarkable removal efficiency, with fly ash removing over 97% of direct blue 78 dye at doses ranging from 3 g/L to 5 g/L. At the same time, Chen et al. (2021) reported that treated fly ash exhibited substantial removal rates, with removal efficiencies of 74.37% for Pb²⁺ and 82.71% for Cd²⁺.

Fly ash is readily available, reusable, low-cost, and environmentally sustainable (Ramesh et al., 2016). By assisting in their recycling, the inexpensive adsorbents also aid in addressing the issue of solid waste products in the environment. As a result, it is worthwhile to investigate further how fly ash can be used in various situations. Our study fills a crucial gap by investigating the impact of various pretreatments on the adsorption performance of fly ash for different heavy metal ions. Surprisingly, there is limited research comparing these aspects. It is discovered that pretreatment doesn't universally ensure superior adsorption, emphasizing the need for tailored approaches. Therefore, this study aimed to (1) investigate the adsorption capacity of fly ash by using untreated and chemical treated (using HCl and NaOH) in removing Cr, Cu, Ni, and Zn ions from aqueous solution, and (2) analyse the adsorption capacity of different pretreatments of fly ash in removing various metal ions from solution by isotherm models.

RESEARCH METHODOLOGY

Materials

In this study, fly ash (FA) was collected from Jimah Power Plant which is located at Port Dickson, Negeri Sembilan. It was washed thoroughly with distilled water to remove the impurities and oven dried at 120 °C for 24 h. After that, the fly ash was allowed to cool at room temperature prior to being sieved to 250 µm. The fly ash was later separated into three batches, the first batch was an untreated sample and the other two batches were treated by using 0.5 mol of sodium hydroxide (NaOH) and 0.5 mol of hydrochloric acid (HCl). In the pretreatment phase, 72 g of fly ash were immersed separately in two distinct beakers containing 0.5 mol of NaOH and 0.5 mol of HCl solutions for 24 h as depicted in Figure 1. Both chemicals treated fly ash were subsequently filtered and rinsed with distilled water to eliminate the excess NaOH and HCl from the surface. The pretreated fly ash was then dried at 105 °C for 24 h for further use.



Figure 1: Fly ash soaked in HCl and NaOH

Preparation of Stock Solution

The stock solution of Cr (VI), Cu (II), Ni, and Zn (II) ions with a concentration of 100 mg/L was prepared separately by using chromium (VI) oxide, copper (II) oxide, nickel (II) chloride, and zinc oxide in accordance with EPA Method 6010 D. The pH value of the stock solution was adjusted by adding 0.1 mol of NaOH and 0.1 mol of HCl (Naiya and Das, 2016).

Adsorption Experiment

This adsorption experiment was conducted by using a jar test apparatus with a maximum of 6 beakers in a batch. A series of jar test experiments were carried out by placing 100 mL of Cr, Cu, Ni, and Zn ions aqueous solution with a fixed concentration of 100 mg/L. Then, 3g of untreated fly ash was added to each beaker. The pH value of the solution was adjusted to the desired value of pH 7 by using 0.1M HCl or 0.1M NaOH. The experiment process involved two stages which were rapid mixing for 3 min at 160 rpm and followed by a slow mixing for

17 min at 40 rpm. Figure 2 demonstrates one of the settings in the Jar test. Next, water sample was collected for 60 min, 90 min, 120 min, 150 min, 180 min, and 210 min for testing and analysing the final concentration for each heavy metal. The aforementioned steps were repeated by using acid-treated and alkaline-treated fly ash.



Figure 2: Jar test apparatus and setting

Analytical Method

In this study, the percentage removal for heavy metal ions and the adsorption capacity of the various pretreated fly ash were first calculated and estimated by using Equation 1 and Equation 2, respectively (Rondón et al., 2013). Then, the adsorption isotherm models, such as Langmuir, Freundlich, Temkin, Brunauer-Emmett-Teller (BET), and Dubinin Radushkevich (D-R) isotherm models were further analysed for the experimental data to describe the adsorptive isotherm performed in the adsorbent to the adsorbate. The suitability of these models to the experimental data was later praised by the regression coefficients (R^2) based on the formation of linear graphs (Ohale et al., 2020). Table 1 shows the various adsorption isotherm models used for the study.

Table 1: The adsorption isotherm models used for this study.

Analytical methods	Equations	
Percentage removal	$\%R = \frac{c_0 - c_e}{c_0} \times 100$	(1)
Adsorption capacity	$q_e = \frac{(c_0 - c_e) \times V}{m}$	(2)
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L}$	(3)
Freundlich	$\text{Log } q_e = \text{Log } K_f + \frac{1}{n} \text{Log } C_e$	(4)
Temkin	$q_e = B \ln K_T + B \ln C_e$ and	(5)

		$B = \frac{RT}{b_T}$	(6)
Brunauer-Emmett-Teller (BET)		$\frac{C_e}{q_e(C_s - C_e)} = \frac{(C_{BET} - 1)}{Q_m C_{BET}} \left(\frac{C_e}{C_s}\right) + \frac{1}{Q_m C_{BET}}$	(7)
	and		
		$C_s = C_0 - C_e$	(8)
Dubinin Radushkevich (D-R)		$\ln \ln q_e = \ln \ln Q_m - K_{DR} \varepsilon^2$	(9)
	and		
		$\varepsilon = RT \ln \ln \left(1 + \frac{1}{C_e}\right)$	(10)
	and		
		$E_{DR} = 1/\sqrt{2K_{DR}}$	(11)
C_0	Initial concentration of adsorbate (mg/L)		
C_e	Concentration of the adsorbate in the solution at equilibrium (mg/L)		
V	Volume of solution (L)		
m	Weight of adsorbent (mg)		
q_e	Amount of metal ions being adsorbed per specific amount of adsorbent (mg/g)		
Q_m	Maximum adsorption capacity of metal ions (mg/g)		
K_L	Langmuir isotherm constant which is related to the adsorption capacity (L/mg)		
K_f	Freundlich isotherm constant		
n	Adsorption intensity of the adsorbate to adsorbent or surface heterogeneity.		
B	Constant related to heat of sorption (J/mol)		
R	Universal gas constant, (J/mol K)		
T	Absolute temperature (K)		
b_T	Factor related to the interaction between the adsorbent and adsorbate		
K_T	Equilibrium binding constant (L/g)		
C_{BET}	Energy interaction with the surface of the adsorbent		
C_s	Saturation concentration (mg/L) $C_0 - C_e$		
K_{DR}	Dubinin Radushkevich model constant or activity coefficient		
E_{DR}	Removal energy of the adsorbate to adsorbent.		
ε	Polanyi potential		

RESULTS AND DISCUSSION

The results and analysis of the study were presented and discussed in the following sections.

Effectiveness of the various pretreated fly ash in various metal ions removal

The effectiveness of pretreated fly ash (UFA, HCl-FA, and NaOH-FA) in adsorbing various metal ions (Cr, Cu, Ni, and Zn ions) were examined. Figure 3 shows the result obtained for UFA, HCl-FA, and NaOH-fly ash in removing the Cr, Cu, Ni, and Zn ions from the aqueous solution, respectively with an initial concentration of 100 mg/L.

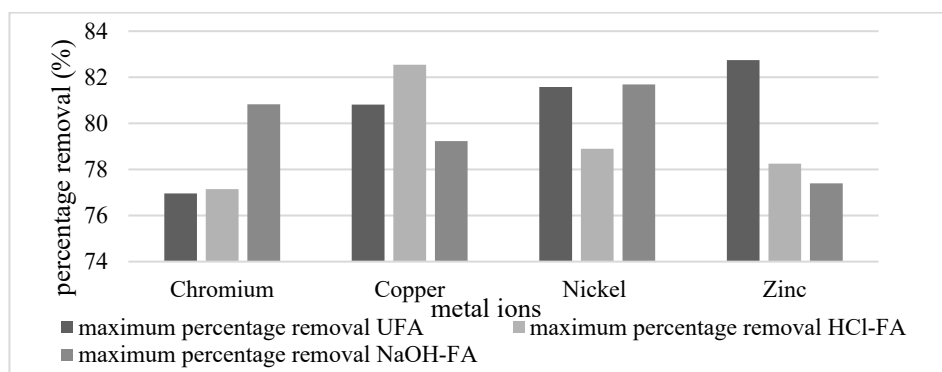


Figure 3: Percentage removal of different pretreated fly ash to Cr, Cu, Ni, and Zn ions solution.

From Figure 3, the maximum percentage removal of Cr ion by UFA was 76.958% on a contact duration of 90 min. HCl-FA achieved a maximum Cr ion removal of 77.148% within a contact duration of 150 min. For alkaline-treated fly ash, the maximum Cr ion removal was 80.828% within 210 min of contact period in an aqueous solution. For the Cu ion solution, UFA was able to adsorb a maximum of 80.814% on contact duration of 120 min. For acid-treated fly ash, the maximum removal percentage for Cu ion was 82.546% at 90 min of contact time, while 79.230% of Cu ion was removed by NaOH-FA within 150 min of contact time. Likewise, for Ni ion, the maximum removal percentage for UFA, HCl-FA, and NaOH-FA were 81.580% at 180 min of contact time, 78.896% at 180 min of contact time, and 81.692% at 150 min of contact time, respectively. For the Zn ion solution, the maximum percentage removal for UFA, HCl-FA, and NaOH-FA were 82.742% at 180 min of contact time, 78.248% at 210 min of contact time, and 77.394% at 180 min of contact time.

The obtained results indicated that the adsorption of metal ions in the aqueous solution exhibited minor fluctuations for each distinct type of fly ash as the contact time varied. This is due to the different surface area of fly ash and led to the amount of free adsorption site. Li et al. (2016) stated that with the continuation of adsorption time, adsorption became more saturated, and solute diffusion to the surfactant concentration was hindered. In addition, there was a slight outperformance of Ni ion removal by NaOH-FA as compared to UFA and HCl-FA, while HCl-FA was slightly better at removing Cu ions from an aqueous solution. Then, the performance in the case of Zn ion by UFA is remarkable as compared to the adsorption performance on other metal ions. This indicated that the functional group of different pretreatments of fly ash have affected the affinity of metal ions onto the fly ash. For instance, the modified FA by NaOH solution increased the surface area and the negative charge of the fly ash (Ranasinghe et al., 2022). According to Alterary and Marei (2021), as pH value increased, the

negatively charged adsorbent was predicted to have a better attraction to the positively charged nickel and chromium ions in the solution. In this scenario, the electrostatic attraction may be the main factor due to the higher pH value in adsorbing metal ions as compared to the lower pH value (Adewoye et al., 2017). To gain a deeper understanding of the adsorption capacity of distinct pre-treated fly ash samples for different metal ions, Figure 4 illustrates the adsorption capacity of these pre-treated fly ash variants in the removal.

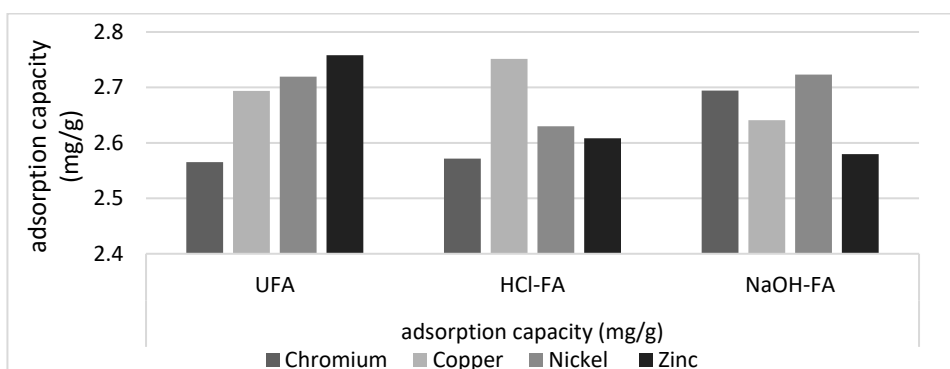


Figure 4: The adsorption capacity of UFA, HCl-FA, and NaOH-FA in various metal ions solutions.

In Figure 4, the results indicate that the adsorption capacities of UFA, HCl-FA, and NaOH-FA are comparable within a similar range of adsorption capacities from 2.5 mg/g to 2.8 mg/g. The maximum adsorption capacity in the order from highest to lowest was 2.7581 mg/g for Zn ion by UFA > 2.7515 mg/g for Cu ion by HCl-FA > 2.7231 mg/g for Ni ion by NaOH-FA > 2.7193 mg/g for Ni ion by UFA > 2.6943 mg/g for Cr ion by NaOH-FA > 2.6938 mg/g for Cu ion by UFA > 2.641 mg/g for Cu ion by NaOH-FA > 2.6299 mg/g for Ni ion by HCl-FA > 2.6083 mg/g for Zn ion by HCl-FA > 2.5798 mg/g for Zn ion by NaOH-FA > 2.5716 mg/g for Cr ion by HCl-FA > 2.5653 mg/g for Cr ion by UFA.

When the fly ash is pretreated with acid or alkali, the chemicals become immobilised at the adsorbent's surface, altering the removal mechanism. It should be emphasised that the removal of metal ions in the solution is induced not only by the adsorbent's porosity but also by the surface attraction or chemical bonding phenomenon caused by the freshly added chemical onto the adsorbent (Qasem, et al., 2021). Table 2 shows the chemical composition of fly ash changes by various pretreatment methods.

Table 2: The chemical composition of fly ash by various pretreatment methods

Constituent	Raw FA	Acid treated FA	Raw FA	Acid treated FA	Raw FA	Alkaline treated FA	Raw FA	Alkaline treated FA
SiO ₂	50.5	60.8	50.96	61.66	60.46	13.74	31.4	10.9
Al ₂ O ₃	26.5	22.2	27.45	24.2	21.50	5.99	28.16	8.6
Fe ₂ O ₃	9.2	6.2	7.02	5.47	4.30	2.79	20.91	4.4
CaO	5.6	2.0	4.22	1.07	7.63	2.69	4.82	1.35
MgO	2.2	0.7	1.28	0.75	0.82	0.23	1.96	0.64
SO ₃	-	-	1.52	0.18	-	-	-	-
TiO ₂	1.6	2.0	1.74	1.92	1.53	0.69	-	-
K ₂ O	1.6	1.7	3.34	3.21	1.25	0.45	0.1	0.12
References	(Go and Yeom, 2019)		(Gjyli et al., 2021)		(Agarwal et al., 2018)		(Santi et al., 2021)	

It was observed that the raw fly ash content was found to be high in aluminosilicate (Si-O-Al). As a result, fly ash is able to perform effectively in adsorbing various metal ions. Increased silica and alumina content through acid pretreatment, as indicated in Table 2, will improve the surface area and sorption characteristics of the fly ash. The stronger the acid, the higher the pH value and surface area of the fly ash and the stronger the interactions of surface functional groups, especially for metal ions such as copper ion, which prefer an alkaline environment (Buema et al., 2021). On the other hand, alkaline treatment increased the soluble Si content while decreasing the alumina and silica content in raw fly ash (Santi et al., 2021). However, the degradation of the mineral surface may be anticipated to enhance the rough surface of the fly ash, resulting in increased porosity of alkaline-treated fly ash capable of metal ion adsorption. Indeed, due to the pH content of the adsorbent to the adsorbate, alkaline treatment exhibited a good performance in removing some of the metal ions as mentioned previously.

Adsorption Isotherms analysis for Cr, Cu, Ni, and Zn ions in solution

Adsorption isotherm models were used in the study to further evaluate the adsorption mechanism of the pollutants into the adsorbent. To investigate the adsorption isotherms, the collected data were analysed by using the Langmuir isotherm, Freundlich, Temkin, BET, and D-R isotherms. Table 3 displays the parameters and correlation coefficients of Langmuir, Freundlich, Temkin, BET, and D-R isotherm models for different heavy metal ions (Cr, Cu, Ni, and Zn) on various fly ash (UFA, HCl-FA, and NaOH-FA), as inferred from the gradient and intercept of the linear graphs.

Table 3: The parameters and correlation coefficients of Langmuir, Freundlich, Temkin, Brunauer-Emmett-Teller (BET), and Dubinin Radushkevich (D-R) isotherm models for different heavy metal ions (Cr, Cu, Ni, and Zn) on various fly ash (UFA, HCl-FA, and NaOH-FA).

	Temkin				Brunauer-Emmett-Teller (BET)		
	K_T (L/g)	B (J/mol)	b_T	R^2	Q_m (mg/g)	C_{BET}	R^2
UFA							
Cr	2.183	-0.859	-2894.604	0.999	1.048	0.846	0.998
Cu	1.948	-0.823	-3019.050	0.994	1.023	0.853	0.985
Ni	1.303	-0.730	-3403.458	0.998	1.264	0.892	0.997
Zn	2.159	-0.848	-2931.469	0.982	0.801	0.810	0.930
HCl-FA							
Cr	2.217	-0.864	-2878.516	0.998	1.029	0.841	0.994
Cu	1.223	-0.717	-3466.099	0.996	1.266	0.893	0.991
Ni	1.529	-0.766	-3243.588	0.999	1.222	0.881	0.999
Zn	1.808	-0.807	-3081.932	0.999	1.138	0.865	0.996
NaOH-FA							
Cr	1.751	-0.797	-3121.012	0.997	1.110	0.866	0.992
Cu	1.629	-0.780	-3186.216	0.999	1.180	0.876	0.997
Ni	0.965	-0.675	-3681.703	0.999	1.397	0.910	0.998
Zn	2.093	-0.847	-2936.664	0.998	1.061	0.849	0.995
Dubinin Radushkevich (D-R)							
	Q_m (mg/g)	EDR	R^2				
UFA							
Cr	2.070	158.114	0.993				
Cu	2.119	158.114	0.942				
Ni	2.251	223.607	0.978				
Zn	2.086	158.114	0.837				
HCl-FA							
Cr	2.068	158.114	0.980				
Cu	2.271	223.607	0.957				
Ni	2.204	223.607	0.992				
Zn	2.145	158.114	0.988				

NaOH-FA			
Cr	2.153	223.607	0.964
Cu	2.178	223.607	0.992
Ni	2.335	235.702	0.986
Zn	2.090	158.114	0.984

The result from Table 3 indicated that all the heavy metal ions adsorption on UFA, HCl-FA, and NaOH-FA were favourable to Temkin isotherm. The accuracy and compatibility of the adsorption system by using the Temkin isotherm can be seen in R^2 value with all the R^2 coefficients of more than 0.99 for all the metal ions and the R^2 coefficient of 0.982 for zinc adsorption. The closer it is to 1, the more compatible it is to the Temkin isotherm model as the assumption of the model coincides with the adsorption system. Table 3 reveals that the regression coefficient value of Temkin isotherm is 0.999 (Cr ions by UFA), 0.994 (Cu ions by UFA), 0.998 (Ni ions by UFA), 0.982 (Zn ions by UFA), 0.998 (Cr ions by HCl-FA), 0.996 (Cu ions by HCL-FA), 0.999 (Ni ions by HCl-FA), 0.999 (Zn ions by HCl-FA), 0.997 (Cr ions by NaOH-FA), 0.999 (Cu ions by NaOH-FA), 0.999 (Ni ions by NaOH-FA), and 0.998 (Zn ions by NaOH-FA). The Temkin isotherm model reflected the interaction between the metal ions in the solution and the fly ash. It is assumed that as more metal ion molecules adhere to the fly ash surface, the heat of adsorption for all molecules in the layer decrease linearly (Elmorsi et al., 2022).

According to the Temkin isotherm model, adsorption is defined by a uniform distribution of binding energies up to a maximum binding energy (Owino et al., 2023). The b_T value in this study ranged from -3681.703 to -2878.516, which was less than 80, indicating that the adsorption process is physical between the metal ions and fly ash (Nandiyanto et al., 2022). Furthermore, the investigation showed the B constant ranging from -0.8636 to -0.6752, implying $B < 8\text{kJ/mol}$, signifying a weak contact between the adsorbate and absorbent, likely due to minimal physical sorption in the initial layer (Elmorsi et al., 2022). Moreover, the negative value of the Temkin constant, B also indicated the endothermic heat adsorption process, as adsorption can be enhanced by increasing temperatures (Potgieter et al., 2021).

The K_T value of the study in the Temkin isotherm model further demonstrated that the adsorption affinity of the metal ions onto the binding sites of fly ash which revealed in the order 2.22L/g (Cr ions by HCl-FA) > 2.18L/g (Cr ions by UFA) > 2.16L/g (Zn ions by UFA) > 2.09L/g (Zn ions by NaOH-FA) > 1.95L/g (Cu ions by UFA) > 1.81L/g (Zn ions by HCl-FA) > 1.75L/g (Cr ions by NaOH-FA) > 1.63L/g (Cu ions by NaOH-FA) > 1.53L/g (Ni ions by HCl-FA) > 1.30L/g (Ni ions by UFA) > 1.22L/g (Cu ions by HCl-FA) > 0.97L/g (Ni ions by NaOH-FA). Principally, numerous factors influence the adsorption affinity

between heavy metal ions and fly ash, such as ionic radii, molecular size, the surface roughness of the fly ash, and the adsorption capacities of the binding groups that react with various metal ions in the solution (Wadhawan et al., 2020). However, the variation of the adsorption affinity of the fly ash is minimal which is less than 1.252 L/g, indicated that both untreated and treated fly ash (acid and alkaline treatments) maintained effective metal ion removal capabilities with only slight impact on the favourability of metal ion adsorption.

CONCLUSION

Based on the study result, both untreated and pretreated fly ash had a significant effect on removing the chromium, copper, nickel and zinc ions from the aqueous solution. The recorded Cr, Cu, Ni, and Zn ions removal rates by UFA were 2.565 mg/g, 2.694 mg/g, 2.719 mg/g, and 2.758 mg/g, respectively. Then, HCl-FA were adsorbed with 2.572 mg/g of Cr ions, 2.752 mg/g of Cu ions, 2.630 mg/g of Ni ions, 2.608 mg/g of Zn ions. While the percentage removal of Cr, Cu, Ni, and Zn ions removal rates by NaOH-FA were 2.694 mg/g, 2.641 mg/g, 2.723 mg/g, 2.580 mg/g, respectively. All the heavy metal ions (Cr, Cu, Ni, and Zn ions) adsorption on UFA, HCl-FA, and NaOH-FA were favourable to Temkin isotherm, with R^2 more than 0.98. Furthermore, the study revealed that all heavy metal ions adsorbed by fly ash were dominated by physical adsorption with an endothermic heat adsorption mechanism. This insight is valuable for water treatment and environmental remediation efforts, providing practical guidance for optimal fly ash utilization based on the target heavy metal ions and water conditions. By bridging the gap between theory and application, this research not only contributes novel findings but also holds the potential to advance current practices in environmental science.

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REFERENCES

- Adewoye, L.T., Mustapha, S.I., Adeniyi, A.G., Tijani, J.O., Amoloye, M.A. & Ayinde, L.J. (2017). Optimization of nickel (ii) and chromium (iii) removal from contaminated water using sorghum bicolor. *Nigerian Journal of Technology*, 36(3), 960-972.
- Agarwal, S., Rajoria, P. & Rani, A. (2018). Adsorption of tannic acid from aqueous solution onto chitosan/NaOH/fly ash composites: Equilibrium, kinetics, thermodynamics and modelling. *Journal of environmental chemical engineering*, 6(1), 1486-1499.

- Alsaffar, M.S., Suhaimi, J.M. & Ahmad, K.N. (2019). Evaluation of heavy metals in surface water of major rivers in Penang, Malaysia. *International Journal of Environmental Science*, 6(5), 657-669.
- Alterary, S.S. & Marei, N.H. (2021). Fly ash properties, characterization, and applications: A review. *Journal of King Saud University-Science*, 33(6), p.101536.
- Beddu, S., Zainoodin, M., Kamal, N.M., Mohamad, D., Nabihah, S. & Nazri, F.M. (2018). Material characterization of coal combustion product (cenosphere) generated from coal-fired power plant in Malaysia. *In AIP Conference Proceedings*, 2030 (1). AIP Publishing.
- Buema, G., Harja, M., Lupu, N., Chiriac, H., Forminte, L., Ciobanu, G., Bucur, D. & Bucur, R.D. (2021). Adsorption performance of modified fly ash for copper ion removal from aqueous solution. *Water*, 13(2), p.207.
- Chen, X., Zhang, G., Li, J., & Ji, P. (2021). Possibility of removing Pb and Cd from polluted water by modified fly ash. *Adsorption Science & Technology*, 2021, 1-8.
- Darmayanti, L., Notodarmodjo, S., Damanhuri, E. & Mukti, R.R. (2018). Removal of copper (II) ions in aqueous solutions by sorption onto alkali activated fly ash. *In MATEC Web of Conferences*, 147, EDP Sciences, p. 04007.
- De Maeijer, P.K., Craeye, B., Snellings, R., Kazemi-Kamyab, H., Loots, M., Janssens, K. & Nuyts, G. (2020). Effect of ultra-fine fly ash on concrete performance and durability. *Construction and Building Materials*, 263, p.120493.
- Elmorsi, R.R., Abou-El-Sherbini, K.S., Shehab El-Dein, W.A. & Lotfy, H.R. (2022). Activated eco-waste of *Posidonia oceanica* rhizome as a potential adsorbent of methylene blue from saline water. *Biomass Conversion and Biorefinery*, 1-14.
- Eteba, A., Bassyouni, M., & Saleh, M. (2021). Removal of hazardous organic pollutants using fly ash. *Environ. Ecol. Res*, 9, 196-203.
- Ghazali, N., Muthusamy, K. & Wan Ahmad, S. (2019). Utilization of Fly Ash in Construction. *IOP Conference Series: Materials Science and Engineering*, 601, p. 012023.
- Gjyli, S., Korpa, A., Teneqja, V., Siliqi, D. & Belviso, C. (2021). Siliceous fly ash utilization conditions for zeolite synthesis. *Environmental Sciences Proceedings*, 6(1), p.24.
- Go, Y.W. and Yeom, S.H. (2019). Fabrication of a solid catalyst using coal fly ash and its utilization for producing biodiesel. *Environmental Engineering Research*, 24(2), 324-330.
- Goi, C.L. (2020). The river water quality before and during the Movement Control Order (MCO) in Malaysia. *Case Studies in Chemical and Environmental Engineering*, 2, p.100027.
- Habibullah, N., Sahrir, S., & Ponrahono, Z. (2023). Integrating Rainwater Harvesting And Greywater Recycling To Increase Water Efficiency In Office Buildings. *PLANNING MALAYSIA*, 21(5), 253-266.
- Li, J., Gan, J., Wang, G., Chen, Z. & Gong, Y. (2016). Research on adsorbent using modified fly ash for campus domestic sewage treatment. *In MATEC Web of Conferences*, 67, EDP Sciences, p. 07003.
- Mardi, N.H., Ean, L.W., Malek, M.A., Chua, K.H. & Ahmed, A.N. (2023). Operational blue water footprint and water deficit assessment of coal-fired power plants: case study in Malaysia. *Environmental Sciences Europe*, 35(1), 1-15.

- Naiya, T.K. & Das, S.K. (2016). Removal of Cr (VI) from aqueous solution using fly ash of different sources. *Desalination and Water Treatment*, 57(13), 5800-5809.
- Nandiyanto, A.B.D., Girsang, G.C.S. & Rizkia, R.S. (2022). Isotherm adsorption characteristics of 63-um calcium carbonate particles prepared from eggshells waste. *Journal of Engineering Science and Technology*, 17 (5), 3203-3210.
- Nguyen, D. H. (2020). Itai-Itai disease: the role of mining in the degradation of Japanese society and public health (Doctoral dissertation, The Ohio State University).
- Nguyen, T. C., Tran, T. D. M., Dao, V. B., Vu, Q. T., Nguyen, T. D., & Thai, H. (2020). Using modified fly ash for removal of heavy metal ions from aqueous solution. *Journal of Chemistry*, 2020, 1-11.
- Ohale, P.E., Onu, C.E., Ohale, N.J. & Oba, S.N. (2020). Adsorptive kinetics, isotherm and thermodynamic analysis of fishpond effluent coagulation using chitin derived coagulant from waste *Brachyura* shell. *Chemical Engineering Journal Advances*, 4, p.100036.
- Othman, F., Uddin Chowdhury, M.S., Wan Jaafar, W.Z., Mohammad Faresh, E.M. & Shirazi, S.M. (2018). Assessing Risk and Sources of Heavy Metals in a Tropical River Basin: A Case Study of the Selangor River, Malaysia. *Polish Journal of Environmental Studies*, 27(4), 1659-1671.
- Owino, E.K., Shikuku, V.O., Nyairo, W.N., Kowenje, C.O. & Otieno, B. (2023). Valorization of solid waste incinerator fly ash by geopolymer production for removal of anionic bromocresol green dye from water: Kinetics, Isotherms and Thermodynamics studies. *Sustainable Chemistry for the Environment*, p.100026.
- Potgieter, J.H., Pardesi, C. & Pearson, S. (2021). A kinetic and thermodynamic investigation into the removal of methyl orange from wastewater utilizing fly ash in different process configurations. *Environmental Geochemistry and Health*, 43, 2539-2550.
- Qasem, N. A., Mohammed, R. H., & Lawal, D. U. (2021). Removal of heavy metal ions from wastewater: A comprehensive and critical review. *Npj Clean Water*, 4(1), 36.
- Ramesh, S., Sudarsan, J.S. & Jothilingam, M. (2016). Low cost natural adsorbent technology for water treatment. *Rasayan Journal of Chemistry*, 9(3), 325-330.
- Ranasinghe, R. A. J. C., Hansima, M. A. C. K., & Nanayakkara, K. G. N. (2022). Adsorptive removal of fluoride from water by chemically modified coal fly ash: Synthesis, characterization, kinetics, and mechanisms. *Groundwater for Sustainable Development*, 16, 100699.
- Rondón, W., Freire, D., de Benzo, Z., Sifontes, A.B., González, Y., Valero, M. & Brito, J.L. (2013). Application of 3A zeolite prepared from Venezuelan kaolin for removal of Pb (II) from wastewater and its determination by flame atomic absorption spectrometry. *American Journal of Analytical Chemistry*, 4(10), 584-593.
- Salleh, H., Ying, C. K., Hanid, M., Samad, Z. A., Sabli, N. A. M., & Khuzzan, S. M. S. (2022). Development Of Guidance For The Adoption Of Circular Economy In Construction And Demolition Waste Management. *PLANNING MALAYSIA*, 20 (5), 415-427.

- Santi, L.P., Goenadi, D.H., Kalbuadi, D.N. & Sari, I.P. (2021). Alkaline pre-treatment of coal fly ash as bio-silica fertilizer. *Journal of Minerals and Materials Characterization and Engineering*, 9(02), p.180.
- Sylwan, I. & Thorin, E. (2021). Removal of heavy metals during primary treatment of municipal wastewater and possibilities of enhanced removal: A review. *Water*, 13(08), p.1121.
- Tan, Y.H., Chai, M.K., Na, J.Y. & Wong, L.S. (2023). Microalgal Growth and Nutrient Removal Efficiency in Non-Sterilised Primary Domestic Wastewater. *Sustainability*, 15(8), p.6601.
- Feary, J., & Cullinan, P. (2019). Heavy Metals. *Reference Module in Biomedical Sciences [Internet]; Elsevier: Amsterdam, The Netherlands*.
- Wadhawan, S., Jain, A., Nayyar, J. & Mehta, S.K. (2020). Role of nanomaterials as adsorbents in heavy metal ion removal from waste water: A review. *Journal of Water Process Engineering*, 33, p.101038.
- World Health Organization, WHO (2023). Humanitarian emergencies - Water Sanitation and Health. Health risks: Drinking-water and sanitation. Retrieved from: <https://www.who.int/teams/environment-climate-change-and-health/water-sanitation-and-health/environmental-health-in-emergencies/humanitarian-emergencies>

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